VERIFICATION OF TRANSLATION

Re: U.S. PATENT APPLICATION SERIAL NO. 60/498,867

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hereby declare that I am the translator of the document attached and certify that the following is true translation to the best of my knowledge and belief.

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Title

Heat resistant label applicable under high temperature

LICENSE FOR FOREIGN FILING UNDER
Title 35, United States Code, Section 184
Title 37, Code of Federal Regulations, 5.11 & 5.15

GRANTED

Specification

HEAT RESISTANT LABEL APPLICABLE UNDER HIGH TEMPERATURE

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

The present invention relates to compositions for heat-resistant labels that are attachable at high temperature conditions of 300 °C or higher, heat-resistant labels, products with the labels attached, and methods for producing the labels.

DESCRIPTION OF THE RELATED ART

In various industrial fields, such as food, machinery and chemicals, a label on which symbols, letters, patterns, etc., have been printed, i.e., a patterned label, is attached to products or their packaging materials to control the production process. A typical example of such process control is a system utilizing labels on which a bar-code is printed. In a bar-code control system, data such as production conditions, production managers, production period, destination, and product price are read from the bar-code label by a bar-code reader to control production, sales, and distribution.

The bar-code labels that are currently in wide use are made by producing a resin or paper label having poor

heat resistance, and then applying an adhesive made of acrylic resin or the like to it. However, because both the label and the adhesive decompose and evaporate at temperatures of 300°C or higher, they cannot be used in industries requiring high-temperature processing, such as ceramics, metals, and the like. Japanese Patent No. 2614022 discloses heat-resistant labels but does not disclose attaching the labels at such high temperatures. Japanese Unexamined Patent Publication No. 2003-126911 discloses labels to be subjected to a heating process in which an aluminum coil is baked but discloses in Comparative Example 3 in the specification that the information on the label becomes unclear unless the attachment temperature is 150°C or lower.

Therefore, in the metal mining industry, labels for product management are attached to metal products after the melted and formed metal is cooled to a temperature (generally, near room temperature) in the range in which the labels can be attached. The same applies to the ceramics and glass industries, and other industries requiring high-temperature processing.

SUMMARY OF THE INVENTION

However, if label attachment must be waited until metal products are cooled to almost room temperature, time,

energy and space required for cooling such products need to be ensured. For efficient production of metal products, labels attachable at higher temperatures have been in demand to perform product management at earlier stage. Accordingly, an object of the present invention is to provide a heat-resistant label attachable at high temperatures.

The present inventors carried out extensive research to achieve the above-mentioned objects in view of the problems of the prior art. As a result, they found that heat-resistant labels having as a sticking layer a hardened coating film made of a composition comprising a polymetallocarbosilane resin (A); a silicone resin (B); a solvent (C); and optionally an inorganic powder (D) can be attachable at high temperatures.

The present invention thus relates to the following.

Item 1:

A composition for a heat-resistant label comprising a polymetallocarbosilane resin (A), a silicone resin (B), and a solvent (C), wherein the weight ratio of the polymetallocarbosilane resin (A) : the silicone resin (B) is about 1 : about 9 to about 9 : about 1.

Item 2:

A composition for a heat-resistant label further comprising an inorganic powder (D), wherein the inorganic

powder (D) is contained in a ratio of about 0.0001 to about 80 % by weight.

Item 3:

A composition for a heat-resistant label according to claim 1 or 2, wherein the weight ratio of the polymetallocarbosilane resin (A) : the silicone resin (B) is about 3:about 7 to about 8:about 2.

Item 4:

A composition for a heat-resistant label according to any one of claims 1 to 3, wherein the polymetallocarbosilane resin (A) has a weight-average molecular weight of about 500 to about 10000.

Item 5:

A composition for a heat-resistant label according to any one of claims 1 to 4, wherein the silicone resin (B) has a weight-average molecular weight of about 200 to about 5000000.

Item 6:

A composition for a heat-resistant label according to any one of claims 1 to 5, wherein the polymetallocarbosilane resin (A) is a polytitanocarbosilane resin.

Item 7:

A heat-resistant label comprising a sticking layer of a hardened coating film obtained by applying a

composition according to any one of claims 1 to 6 to one side of a support, and evaporating off the solvent contained in the composition.

Item 8:

A heat-resistant label according to claims 7, wherein the sticking layer has a thickness of about 5 μm to about 100 μm.

Item 9:

A heat-resistant label according to claim 7 or 8, wherein the support has a thickness of about 5 μm to about 100 μm.

Item 10:

A heat-resistant label according to any one of claims 7 to 9, wherein the support is an aluminum foil, stainless steel foil, or copper foil.

Item 11:

A heat-resistant label according to any one of claims 7 to 10 having a heat-resistant label base layer on the other side of the support.

Item 12:

A heat-resistant label according to claim 11, wherein the label base layer has a thickness of about 0.5 μm to about 100 μm.

Item 13:

A heat-resistant label according to claims 11 or

12, wherein the label base layer is a cured coating film obtained by crosslinking the resin in the composition according to any one of claims 1 to 6.

Item 14:

A heat-resistant label according to any one of claims 11 to 13 having an identification part on the label base layer.

Item 15:

An article to which a heat-resistant label of any one of claims 7 to 14 is attached through a cured sticking layer.

Item 16:

A method for producing a heat-resistant label comprising the steps of:

applying a composition of any one of claims 1 to 6 to one side of a support; and

drying the applied composition to form a hardened coating film.

Item 17:

A production method according to claim 16, wherein the applied composition is dried at about 50 °C to about 240 °C.

Item 18:

A production method according to claim 16 or 17, comprising, prior to the step of applying a composition of

any one of claims 1 to 6 to one side of a support, the steps of:

applying a composition for a heat-resistant label base layer to the other side of the support; and

drying the applied composition to form a cured coating film.

Item 19:

A production method according to any one of claims 16 to 18, wherein the composition for a label base layer is a composition of any one of claims 1 to 6.

DETAILED DESCRIPTION OF THE INVENTION

Compositions for heat-resistant labels of the present invention comprise a polymetallocarbosilane resin (A), a silicone resin (B), and a solvent (C), and wherein the weight ratio of the polymetallocarbosilane resin (A) : the silicone resin (B) is about 1 : about 9 to about 9 : about 1.

The polymetallocarbosilane resin (A) contained in the composition of the invention enables label attachment at high temperatures. The polymetallocarbosilane resin (A) has a crosslinked structure obtained by, for example, reacting polycarbosilane with metal alkoxide. Examples of the above-mentioned metal include titanium, zirconium, molybdenum, chromium, etc., and among these titanium and zirconium are

preferable. Preferred examples of the polymetallocarbosilane resin are polytitanocarbosilane resins, polyzirconocarbosilane resins, etc. As a mixture comprising the polytitanocarbosilane resin, for example, a "Tyranno coat VS-100", "Tyranno coat VN-100", etc. manufactured by Ube Industries, Ltd., can be used. The weight-average molecular weight of the polymetallocarbosilane resin is preferably about 500 to about 10000, and more preferably about 700 to about 3000.

In the invention, the silicone resin (B) has a polyorganosiloxane structure in its molecule. Examples of silicone resins include straight silicone resins and modified silicone resins. Such silicone resins may be used in combination. Preferable is straight silicone resins. These resins can be used as they are, or in the form of a solvent solution. In order to facilitate the process of applying the resin to a support during the label preparation, the resin is preferably used in the form of a solvent solution.

The weight-average molecular weight of such silicone resins are generally about 200 to about 5000000, and preferably about 1000 to about 1000000.

A straight silicone resin includes an organopolysiloxane comprising a hydrocarbon group as a main organic group. The organopolysiloxane may contain a

hydroxyl group. The foregoing hydrocarbon groups can be divided into aliphatic hydrocarbon groups and aromatic hydrocarbon groups. Preferred among these are C_{1-5} aliphatic hydrocarbon groups and C_{6-12} aromatic hydrocarbon groups. Such hydrocarbon groups may be used singly or in combination.

Examples of the C_{1-5} aliphatic hydrocarbon groups include methyl, ethyl, propyl, butyl, pentyl, vinyl, allyl, propenyl, butenyl, and pentenyl groups. Examples of the C_{6-12} aromatic hydrocarbon groups include phenyl, methylphenyl, ethylphenyl, butylphenyl, tertiary butylphenyl, naphthyl, styryl, allylphenyl, and propenylphenyl groups.

The straight silicone resin may be obtained by hydrolyzing one or more silane compounds such as a chlorosilane or alkoxysilane comprising the foregoing aliphatic hydrocarbon group or aromatic hydrocarbon group, and then condensing the hydrolysis products, or by hydrolyzing a mixture of the foregoing silane compound with tetrachlorosilane or tetraalkoxysilane, and then co-condensing the hydrolysis product.

Examples of the foregoing chlorosilane compounds include methyltrichlorosilane, dimethyldichlorosilane, trimethylchlorosilane, methylethyldichlorosilane, vinylmethyldichlorosilane, vinyltrichlorosilane, phenyltrichlorosilane, diphenyldichlorosilane, methylphenyldichlorosilane, vinylphenyldichlorosilane, etc.

Examples of the foregoing alkoxysilane compounds include methyltrimethoxysilane, dimethyldiethoxysilane, trimethylmethoxysilane, vinylmethylmethoxysilane, vinyltributoxysilane, phenyltriethoxysilane, diphenyldimethoxysilane, methylphenyldipropoxysilane, vinylphenyldimethoxysilane, etc.

The modified silicone resin is an organopolysiloxane containing an organic group other than a hydrocarbon group. Examples of the modified silicone resin include methoxy-containing silicone resins, ethoxy-containing silicone resins, epoxy-containing silicone resins, alkyd resin-modified silicone resins, acrylic resin-modified silicone resins, polyester resin-modified silicone resins, epoxy resin-modified silicone resins, etc.

These modified silicone resins can be obtained by, for example, reacting the hydroxyl group of the foregoing straight silicone resin with an organic compound having a functional group reactive to the hydroxyl group, such as carboxyl, acid anhydride, hydroxyl, aldehyde, epoxy, and chloride groups; by copolymerizing a straight silicone resin containing an unsaturated hydrocarbon group, such as a vinyl group, with a compound having an unsaturated double bond; by hydrolyzing a modified silane compound obtained by the reaction of the foregoing silane compound with another organic compound so that it undergoes condensation or co-

condensation, or the like. The organic compound to be reacted may be a low molecular weight compound or a high molecular weight compound such as a resin.

Examples of the silicone resin (B) include dimethylpolysiloxane, methylphenylpolysiloxane, diphenylmethylphenylsilicone resins, etc.

The weight ratio of the polymetallocarbosilane resin (A) : the silicone resin (B) is about 1 : about 9 to about 9 : about 1, and preferably about 3 : about 7 to about 8 : about 2. The composition obtained by mixing these two resins within such a range enables label attachment under high temperature conditions. Further, the total amount of both resins is preferably about 5 to about 50 % by weight, and more preferably about 10 to about 45 % by weight.

In the invention, the solvent (C) has a function of dissolving or dispersing components in the composition to adjust the viscosity thereof. Usable as the solvent (C) are, for example, toluene, xylene, cellosolve acetate, ethyl acetate, butyl carbitol, MEK (methyl ethyl ketone), MIBK (methyl isobutyl ketone), etc. Among these, xylene and toluene are preferable. The proportion of the solvent (C) is not limited insofar as a heat-resistant label can be produced using the composition of the invention. Thus, the proportion of the solvent (C) can be appropriately adjusted in such a manner that the viscosity of the composition of

the invention is suitable for application to the support and drying. The proportion of the solvent (C) is usually about 15 to about 70 % by weight, and preferably about 20 to about 50 % by weight.

In the invention, the heat-resistance of the heat-resistant label can be enhanced by mixing an inorganic powder (D) since thermal expansion and shrinkage of the heat-resistant label can be thereby reduced. Thus, an inorganic powder (D) is preferably mixed with the composition of the invention. The label base layer can be colored by using a color pigment as the inorganic powder (D). Such inorganic powder (D) can be used singly or in combination. The particle diameter is preferably about 0.01 μm to about 200 μm, and more preferably about 0.1 μm to about 100 μm. The inorganic powder (D) is not limited in shape. The inorganic powder (D) is usually contained in a ratio of about 0.0001 to about 80 % by weight, and preferably about 1 to about 65 % by weight in the composition of the present invention.

An inorganic pigment is used preferably as the inorganic powder (D). For example, usable are white substances, such as silica, titanium dioxide, alumina, zirconia, mica, calcium oxide, zinc sulfide-barium sulfate (lithopone), calcium carbonate, etc. Moreover, usable are metal compounds, such as carbonates, nitrates, sulfates,

etc., which are oxidized to form such white substances in a heat treatment during the production of the heat-resistant label. Also, usable as the inorganic powder (D) are reddish-brown substances containing metal ion such as iron, copper, gold, chromium, selenium, zinc, manganese, aluminum, tin, etc. (e.g., zinc oxide-iron oxide-chromium oxide, manganese oxide-alumina oxide, chromium oxide-tin oxide-iron oxide, etc.); blue substances containing metal ion such as manganese, chromium, aluminum, cobalt, copper, iron, zirconia, vanadium, etc. (e.g., cobalt oxide-aluminum oxide, cobalt oxide-aluminum oxide-chromium oxide, cobalt oxide, zirconia-vanadium oxide, chromium oxide-divanadium pentoxide, etc.); black substances containing metal ion such as iron, copper, manganese, chromium, cobalt, aluminum, etc. (e.g., copper oxide-chromium oxide-manganese oxide, chromium oxide-manganese oxide-iron oxide, chromium oxide-cobalt oxide-iron oxide-manganese oxide, chromate, permanganate, etc.); yellow substances containing metal ion such as vanadium, zinc, tin, zirconium, chromium, titanium, antimony, nickel, praseodymium, etc. (e.g., titanium oxide-antimony oxide-nickel oxide, titanium oxide-antimony oxide-chromium oxide, zinc oxide-iron oxide, zirconium-silicon-praseodymium, vanadium-tin, chromium-titanium-antimony, etc.); green substances containing metal ion such as chromium, aluminum, cobalt, calcium, nickel, zinc, etc. (e.g., titanium oxide-

zinc oxide-cobalt oxide-nickel oxide, cobalt oxide-aluminum oxide-chromium oxide-titanium oxide, chromium oxide, cobalt-chromium, alumina-chromium, etc.); pink substances containing metal ion such as iron, silicon, zirconium, aluminum, manganese, etc. (e.g., aluminum-manganese, iron-silicon-zirconium, etc.). Among these, preferable are titanium dioxide, alumina, zinc oxide-iron oxide-chromium oxide, titanium oxide-antimony oxide-nickel oxide, titanium oxide-antimony oxide-chromium oxide, zinc oxide, iron oxide, zinc oxide-iron oxide-chromium oxide, titanium oxide-zinc oxide-cobalt oxide-nickel oxide, cobalt oxide-aluminum oxide-chromium oxide, cobalt oxide-aluminum oxide, cobalt oxide-aluminum oxide-chromium oxide, copper oxide-chromium oxide-molybdenum oxide, copper oxide-chromium oxide-manganese oxide, copper oxide-manganese oxide-iron oxide.

A dispersant (E) is preferably mixed into the composition for heat-resistant labels of the invention. This is because the dispersion rate is improved by mixing a dispersant, thereby facilitating preparation of the composition.

Usable as the dispersant (E) are aliphatic polyvalent carboxylic acids, amine salts of polyester acids, long-chain amine salts of polycarboxylic acids, amine salts of polyether ester acids, amine salts of polyether phosphates, polyether phosphates, amide amine salts of

polyester acids, etc. The dispersant is used in a proportion of about 0.01 to about 5 % by weight, preferably about 0.1 to about 2 % by weight in the composition of the invention.

Additives, such as crosslinking agents, plasticizers, etc., can also be added as needed to the composition for heat-resistant labels of the invention within ranges that do not adversely affect the effects of the invention, in addition to the polymetallocarbosilane resin (A), the silicone resin (B), the solvent (C), inorganic powder (D), and the dispersant (E).

Examples of crosslinking agents include boric acid compounds, organometallic compounds, etc. Boric acid compounds are compounds containing a boric acid residue in its molecule, and include boric acids, borates, borate esters, etc. Boric acids include orthoboric acid, metaboric acid, anhydrous boric acid, etc. Borates include sodium borate, potassium borate, magnesium borate, calcium borate, zinc borate, aluminum borate, etc. Borate esters include methyl borate, ethyl borate, butyl borate, octyl borate, dodecyl borate, etc. Among such boric acid compounds, orthoboric acid is particularly preferable.

Examples of organometallic compounds include organonickel compounds, organoiron compounds, organocobalt compounds, organomanganese compounds, organotin compounds,

organolead compounds, organozinc compounds, organoalumminum compounds, organotitanium compounds, etc., and among these, chelate compounds are preferable. Crosslinking agents are preferably mixed in an amount such that the amount of metal contained in the crosslinking agent is about 0.05 to about 10 parts by weight, preferably about 0.1 to about 5 parts by weight, per 100 parts by weight of the total amount of the resin (A) and the resin (B).

Examples of plasticizers include aliphatic esters, aromatic esters, phosphate esters, etc. Specific examples of aliphatic esters include methyl laurate, butyl oleate, diethylene glycol dilaurate, di(2-ethylbuthoxyethyl) adipate, etc. Specific examples of aromatic esters include dimethyl phthalate, dioctyl phthalate, di(2-ethylhexyl) phthalate, dilauryl phthalate, oleyl benzoate, phenyl oleate, etc. Specific examples of phosphate esters include tricresyl phosphate, trioctyl phosphate, etc. The addition of such plasticizers can provide a further improvement in the flexibility of the label base layer.

The composition of the invention can be prepared by mixing the above-mentioned components. The composition of the invention can also be used as a starting material for the sticking layer of the heat resistant label of the invention. More specifically, the sticking layer is formed

by applying the composition of the invention to one side of a support, and drying the applied composition until the solvent in the composition is removed so as to form a hardened coating film. The composition of the invention can also be used as a starting material for forming the label base layer of the heat-resistant label of the invention. More specifically, the label base layer is formed by applying the composition of the invention to one side of the support, and drying the applied composition at a temperature at which the resins in the composition are crosslinked in such a manner as to form a cured coating film.

In this specification, a hardened coating film represents a film which is obtained by drying the composition of the invention until the solvent in the composition is substantially removed, and which can function as a sticking layer at temperatures of 300°C or higher. Crosslinking of the resins may proceed in such a manner that functionality as the sticking layer is demonstrated. Any remaining solvent might raise the possibility of ignition under high temperature conditions. Therefore, the amount of solvent remaining in the hardened coating film is usually about 0.1% by weight or less, preferably 0.0001% by weight or less. Crosslinking of the resins in the composition may occur in the drying process for removing the solvent. In the case of excessive crosslinking thereof, the film is

cured, and thus the sticking ability is lost under high temperature conditions. Therefore, it is important to conduct the drying process under the drying conditions for forming the hardened coating film where the solvent is removed and the sticking function is maintained even under high temperature conditions, even if crosslinking proceeds.

In this specification, a cured coating film represents a film which is obtained by drying the composition of the invention until the solvent therein is substantially removed, and the film is cured to an extent that it does not adhere to a label attaching machine and, if carries with an identification part, the identification part is kept, at high temperatures of 300 °C or higher in the attachment process. In order to avoid the film from sticking to the label attaching machine, the crosslinking needs to be facilitated to cure the film. Thus, the heating conditions for forming the cured coating film needs to be more severe than those for the hardened coating film.

The heat-resistant label of the invention comprises a sticking layer composed of a hardened coating film obtained by applying the foregoing composition of the invention, and evaporating off the solvent contained in the composition. Alternatively, a heat-resistant label base layer can be provided on the other side of the

support, on which no sticking layer is provided. When a label base layer is not provided, an identification part, such as a bar code or the like, can be provided directly onto the support.

The support of the invention is made of a film-like and heat-resistant material, and a metal foil is preferable. A support made of the same material as the label attaching target gives the label a comparatively high resistance against thermal expansion and shrinkage. Examples of metal foils include aluminum foil, stainless steel foil, copper foil, iron foil, etc. Among these, the aluminum foil is preferably used as the support. However, aluminum foil is likely to be fused at temperatures of 660 °C or higher, and therefore stainless steel foil is preferably used. The thickness of the support is usually about 5 to about 100 μm. When the thickness of the support is within such a range, thermal expansion or thermal contraction is effectively suppressed, and furthermore, the support can be flexible. The support thickness of about 10 to about 40 μm is even more preferable.

Examples of aluminum foils include JIS (Japanese Industrial Standard) alloys 1N30, 1085, 1N90, 1N99, 3003, 3004, 5052, 8079, and 8021, etc., with 1N30 being preferable.

Examples of stainless steel include martensite-

based (SUS410, SUS440), ferrite-based (SUS430, SUS444), austenite-based (SUS304, SUS316), two-sided based (SUS329J1, SUS329J4L) foils, SUS630, and SUS631, etc. Among these, preferable is austenite-based stainless steel, which is free of magnetic properties.

JIS SPHC, SPCC, SECC, SGCC, SZACC, SA1C, etc. can be used as other metals, and among these, SPHC and SPCC Standard are preferable.

Easily available commercial metal foils can be used as the above-described supports.

In the heat-resistant label of the invention, the sticking layer is the above-described hardened coating film. More specifically, such a film is obtained by drying the composition of the invention until the solvent in the composition is at least substantially removed, and serves as a sticking layer under high temperature conditions of 300°C or higher.

The temperature and period for drying the composition of the invention to form the sticking layer are not limited insofar as the composition of the invention is dried and the resultant end product serves as a sticking layer under high temperature conditions. Thus, the temperature and period are appropriately changed according to the thickness and the solvent content of the coating film obtained by applying the composition of the invention, and

material and the thickness of the support. For example, drying may be carried out with a convection oven at about 50 to about 240°C, preferably at about 80 to about 200°C, for about 1 minute to about 60 minutes, and preferably about 1 minute to about 20 minutes. The drying period can be suitably adjusted according to the flow of hot air.

The thickness of the sticking layer after drying is usually about 5 μm to about 100 μm, preferably about 10 μm to about 60 μm. When the dry film thickness of the sticking layer is within such a range, the sticking layer is strongly stuck to the target, thereby inhibiting cohesion failure of the sticking layer.

The heat-resistant label of the invention has a sticking layer on one side of the support, and a heat-resistant label base layer can be formed on the other side of the support. Any conventionally used or reported films obtained by drying compositions for the formation of the label base, such as a composition comprising, for example, a silicone resin, inorganic powder, and organic solvent, can be used as the label base layer insofar as it can withstand temperatures of 300°C or higher. A cured coating film obtained by heating the composition of the invention can also be used as the label base layer. In this case, the label base layer can be formed by applying the composition of the invention to one side of the support and heating the

applied composition until the solvent of the composition is substantially removed and the resins in the composition are crosslinked, so as to form a cured coating film.

When the composition of the invention is used for forming the label base layer, the temperature and period for drying the composition of the invention are not limited insofar as the composition of the invention is dried and the resultant end product serves as the label base layer under high temperature conditions. Thus, the heating temperature and period are appropriately varied according to the thickness and solvent content of the coating film obtained by applying the composition of the invention to the support, and the material and thickness of the support. For example, heating may be carried out with a convection oven at about 245 to about 500°C, preferably at about 250 to about 400°C for about 1 minute to about 40 minutes, preferably about 2 minutes to about 20 minutes. The drying period can be suitably adjusted according to the flow of hot air.

The thickness of the label base layer after heating is generally about 0.5 μm to about 100 μm, and preferably about 1 μm to about 60 μm.

To produce the heat-resistant label with the label base layer obtained by using the composition of the invention, the label base layer is first formed, and subsequently the sticking layer is formed. When the label

layer is formed after the sticking layer, both the layers are made into a cured coating film due to the severer drying conditions for forming the label base layer than those for forming the sticking layer. In such a case, the heat-resistant label cannot be attached under high temperature conditions. When the label base layer is formed using the conventional composition for forming the label base, the order of forming the layers can be suitably determined considering the drying conditions applied to this composition.

The use of a colored label base layer comprising inorganic colored powder permits product management by color classification of the products, if such product management is desired, which eliminates the necessity of having an identification part. However, for more precise product management, it is preferable to provide an identification part on the label base layer. Providing an identification part allows the heat-resistant label to be used as a data carrier. Thus, various information can be given to a product by attaching the label provided with an identification part to the product.

The identification part is usually formed by printing patterns or images, such as characters or symbols (bar codes, etc.), onto the label base layer using known heat-resistant inks. Labels provided with such

identification parts can be used as labels, typified by bar-code labels. Examples of identification parts include any identification codes such as 1-dimensional bar codes of the UPC, JAN (EAN), CODE39, CODE128, ITF, NW-7; 2-dimensional codes of the QR, Micro QR codes; and characters. Among these, 1-dimensional and 2-dimesional bar codes are preferable, and 1-dimensional bar code is more preferable.

Inks capable of withstanding a high-temperature process, i.e., 300°C or higher, is used as the above-mentioned heat-resistant ink. Heat-resistant inks containing a metal oxide, etc. as a color pigment are particularly preferable. Examples of metal oxides for use in the heat-resistant inks include oxides of metals such as iron, cobalt, nickel, chromium, copper, manganese, titanium, aluminum, etc. These can be used singly or mixtures thereof. These metal oxides are supplied in the form of a powder, and the particle size is usually about 0.01 μm to about 50 μm, preferably about 0.1 μm to about 10 μm.

Heat-resistant inks containing such metal oxides can be produced by mixing a binder in an amount of about 1 to about 1000 parts by weight, preferably about 10 to about 200 parts by weight, per 100 parts by weight of the color pigment; adding a solvent as needed; and dispersing or kneading the mixture with a dispersion machine, such as a disper, ball mill, roll mill, sand mill, etc., giving a

liquid-like or paste-like mixture. Examples of the binder for use in the process are resins, waxes, fats, oils, low-melting glasses, etc.

Examples of such resins include silicone resins, hydrocarbon resins, vinyl resins, acetal resins, imido resins, amide resins, acrylate resins, polyester resins, polyurethane resins, alkyd resins, protein resins, cellulose resins, etc. For example, organo polysiloxanes, polymetallocarbosilanes, polystyrene, polyethylene, polypropylene, polyvinyl acetate, polyvinyl butyral, polyvinyl formal, polyimides, polyamides, poly(meth)acrylates, gelatin, cellulose derivatives, polyvinyl alcohol, polyvinyl pyrrolidone, etc. are mentioned. These can be used singly or as mixtures or copolymers thereof.

Examples of waxes include paraffin waxes, natural waxes, higher alcohol waxes, higher amide waxes, higher fatty acids, ester waxes, etc. The following examples may be mentioned: paraffin wax, polyethylene wax, yellow wax, carnauba wax, stearyl alcohol, palmityl alcohol, oleyl alcohol, stearamide, oleamide, palmitamide, ethylenebisstearamide, stearic acid, oleic acid, palmitic acid, myristic acid, ethyl stearate, butyl palmitate, palmityl stearate, stearyl stearate, etc.

Examples of fats and oils are castor oil, soybean

oil, linseed oil, olive oil, beef tallow, lard, mineral oils, etc. Examples of low-melting glasses include glasses with melting points of 700°C or lower, glasses soluble in solvents, and more specifically, a glass frit with the melting point of 700°C or lower and with the particle size of about 0.1 μm to about 100 μm, preferably about 0.2 μm to about 50 μm, water glasses, etc.

The following examples may be mentioned as solvents for use in the process of dispersion or kneading: aliphatic hydrocarbons such as hexane, octane, decane, cyclohexane, etc.; aromatic hydrocarbons such as benzene, toluene, xylene, cumene, naphthalene, etc.; ketones such as acetone, methyl ethyl ketone, cyclohexanone, etc.; alcohols such as methanol, ethanol, 2-ethylhexanol, etc.; ethers such as ethylene glycol monomethyl ether, diethylene glycol dibutyl ether, etc.; esters such as methyl acetate, ethyl formate, ethyl acetoacetate, etc.; petroleum distillation fractions such as gasoline, kerosene, gas oil, etc.; water; etc. It is preferable to use such solvents for dilution in an amount of about 500 parts by weight or less, preferably about 200 parts by weight or less, per 100 parts by weight of the total amount of the metal oxide and binder.

Any patterns, including characters and symbols such as a bar code, may be printed on the heat-resistant label of the invention using the heat-resistant ink composed

of such components by known printing methods, e.g., gravure offset printing, plate offset printing, letterpress printing, intaglio printing, silk screen printing, ink-jet printing, ribbon printing, etc. These may be applied not only when providing the identification part on the label base layer, but also when providing the identification marker directly onto the support.

There is no limitation to the shape of the heat-resistant label of the invention, and a shape suitable for a label attaching machine for attaching the label under high temperature conditions is preferable. The label of the invention can be produced by providing sticking layer and label base layer, if necessary, to the support shaped suitable for attachment to a product, or by producing a large-scale sheet-like support provided with sticking layer and label base layer, if necessary, and then forming the same into a shape suitable for attachment to a product. The forming methods are not limited, and include slit processing, punch processing, etc.

The product of the invention has the heat-resistant label of the invention attached thereon through a cured sticking layer. Any product is included in the invention so long as the heat-resistant label of the invention is attachable, and temperature of products rises to 300 °C or higher, preferably 300 °C to 900 °C during the

production process. Consequently, metal products, ceramics and like heat-resistant products other than a metal billets of steel, aluminum, stainless steel and copper are also included in the invention. Products of the invention include, for example, primary molded products, such as a metal billets of steel, aluminum, stainless steel, copper, etc., slabs, coils, H-shaped steels, cylindrical tubes, rods, plates, etc., and secondary molded products obtained by molding primary molded products by extrusion molding, casting molding, etc.

The method for manufacturing the heat-resistant label of the invention comprises: applying the composition of the invention to one side of the support; and drying the applied composition to form a hardened coating film.

The composition of the present invention is applied to one side of the support by the steps of mixing the composition of the invention and dispersing the mixture using a dispersion machine. Usable examples of dispersion machine include bead mill, disper, ball mill, sand mill, roll mill, etc. Dispersion particle size obtained using dispersion machines is preferably about 0.01 to about 200 μm, and more preferably about 0.1 to about 20 μm.

The thus obtained dispersed composition is applied to one side of the support. Usable examples of application methods include a roll coater method, gravure roll coater

method, doctor blade method, bar coater method, etc., and gravure roll coater method and bar coater methods are preferable. The dispersed composition of the invention is applied to the support, and dried to form a hardened coating film (sticking layer). The drying conditions are the same as those for the sticking layer mentioned above.

The production method of the invention comprises, prior to applying the composition of the invention to one side of the support in the above-mentioned production method: applying the composition for the heat-resistant label base layer to the other side of the support; and heating the applied composition to form a cured coating film.

When the composition of the invention is used as a composition for a heat-resistant label base layer, the step of applying the composition for the heat-resistant label base layer may be carried out in the same manner as the above-described step of applying the composition of the invention. The step of curing the composition of the invention by heating is carried out under the same conditions as the above-described conditions for forming the label base layer.

A conventional composition for a label base layer may be used as the composition for the heat-resistant label base formation. In this case also, the conventional composition can be applied in the same manner as the above-

described step of applying the composition of the invention to one side of the support. In the curing step, the heating conditions can be suitably varied according to the composition used.

The heat-resistant label of the invention can be applied to heat-resistant products in a short time under high temperature conditions, preferably at 300 °C to 900 °C, and therefore the management of heat-resistant products with the use of bar codes, etc. becomes feasible at an earlier stage in the production process. Further, time, energy and space required for cooling metal products and like heat-resistant products to almost room temperature before label attachment can be reduced.

The heat-resistant label of the invention is applicable to heat-resistant products at high temperature status during high-temperature processing or immediately after such processing. In the production of stainless steel billets, the heat-resistant label of the invention is applicable to the stainless steel billets when temperature of the billet once reaches 900 °C down from 1000 °C at the initial stage of its production process. In the production of aluminum billets, the heat-resistant label of the invention is applicable to the billets immediately after the production is finished.

Production management at an earlier stage in the

production thus becomes possible when the label of the invention is applied to metal products, ceramics, and like heat-resistant products other than the metal billets of stainless steel and aluminum mentioned above. If the label of the invention is not peeled off after once applied, it can be used to control sales and distribution management as are the conventional bar-code labels. In the present invention, "products" include not only those distributed in the market after all processing steps, but also materials and intermediate formations in the manufacturing processes.

The present invention is now described below in detail with reference to the following Examples but is not limited thereto. Materials used in Experiments and Comparative Experiments are as follows.

<Support>

Aluminum foil: "1N-30-H-40RT",

40 µm thick,

produced by Nippon Foil Mfg. Co., Ltd.

<Polymetallocarbosilane resin>

"Tyranno coat VS-100"

"Tyranno coat VN-100"

produced by Ube Industries, Ltd.

<Silicone resin>

"KR255" (straight silicone resin),

produced by Shin-Etsu Chemical Co., Ltd.

"TSR116" (straight silicone resin),

produced by GE Toshiba Silicones,

<Inorganic powder>

"TRNS OXIDE RED AA2005"

(Fe_2O_3),

produced by Dainichiseika Color & Chemicals Mfg. Co., Ltd.

<Dispersant>

"Disparlon DA705",

produced by Kusumoto Chemicals, Ltd.

<Heat-resistant ink>

"HP-350A" (containing Fe, Cr, Co, polyester resins and methyl ethyl ketone),

produced by General Corporation.

Rubbing tests were conducted by rubbing an sticking layer or a label base layer at a pressure of 0.5 to 1 kg/cm^2 using 3 to 5 pieces of gauze soaked in xylene. In the rubbing test, when the layer was removed by 5 or 6 rubbings

and adhered to the gauze, the layer was defined as a hardened, and when the layer was not removed by 15 rubbings and had barely adhered to gauze, the layer was defined as a cured.

Example 1

20 parts by weight of Tyranno coat VS-100 as a polymetallocarbosilane resin, 60 parts by weight of KR-380 as inorganic powder, 0.5 parts by weight of Disparon DA705 as a dispersant, and 5 parts by weight of xylene as organic solvent were kneaded. Thereafter, the resultant mixture was dispersed at 3000 rpm for 1 hour using a bead mill dispersion machine ("LMZ-2", manufactured by Ashizawa Finetech Ltd. After confirming the mean particle diameter was 5 μm or less by a grind gauge, a dispersion mill base M-1 was obtained.

20 g of KR255 as a silicone resin was added to 85.5 g of the dispersion mill base M-1, and subsequently 5 g of xylene was added thereto, followed by kneading. Further, xylene was added to the resultant mixture so as to adjust the viscosity to be 25 to 30 seconds/25°C by viscometer using an I.H.S consistency cup (manufactured by Anest Iwata) to form a coating composition. Subsequently, the coat solution was applied to one side of a 40 μm thick aluminum foil using a bar coater so that the dry film thickness was 15 μm, and dried for 10 minutes at 250°C using a convection

oven (ASSF-114S, manufactured by Isuzu Seisakusho Co., Ltd.), and then allowed to stand at room temperature. After confirming the resultant coating film was cured by the rubbing test, a support provided with a label base layer was obtained.

In the next process, the coating composition was applied to the other side of the support with a bar coater so that the dry film thickness was 40 µm, dried at 200°C for 5 minutes using a convection oven (ASSF-114S, manufactured by Isuzu Seisakusho Co., Ltd.), and then allowed to stand at room temperature. After confirming the resultant coating film was hardened by the rubbing test, the coating film was cut into 5 cm × 3 cm pieces, giving heat-resistant labels.

Examples 2 to 13

Heat-resistant labels were prepared using the components and under the drying conditions shown in Tables 1 to 3 in the same manner as in Example 1. In Examples 10 to 12, dispersion was conducted at 3000 rpm for 3 hours, and not 1 hour using a bead mill dispersion machine. In Example 13, a hardened coating film (sticking layer) only was formed onto one side of the support, and no cured coating film (label base layer) was formed.

Comparative Examples 1 to 3

Without label base layer, labels provided with a

sticking layer were obtained using the components and under the drying conditions shown in Table 4 in the same manner as in Example 1.

Table 1

Table 1

		Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5
Composition of the label base layer	TYRANNO COAT VS-100	20	30	30	20	20
	TYRANNO COAT VN-100	-	-	-	-	-
	KR255	20	30	-	-	10
	TSR116	-	-	30	20	10
	KR-380	60	30	30	60	60
	TRNS OXIDE RED AA2005	-	-	-	-	-
	DA705	0.5	0.5	0.5	0.5	0.5
	XYLENE	10	7	13	10	10
Drying condition for the label base layer		250 °C 10 min	250 °C 10 min	250 °C 10 min	250 °C 10 min	250 °C 10 min
Composition of the sticking layer		Same as the label base layer	Same as the label base layer	Same as the label base layer	Same as the label base layer	Same as the label base layer
Drying condition for the sticking layer		200 °C 5 min	200 °C 5 min	200 °C 5 min	200 °C 5 min	200 °C 5 min

Table 2

		Ex. 6	Ex. 7	Ex. 8	Ex. 9	Ex. 10
Composition of the label base layer	TYRANNO COAT VS-100	-	-	-	-	-
	TYRANNO COAT VN-100	40	40	30	30	30
	KR255	-	-	10	10	10
	TSR116	-	-	-	10	10
	KR-380	20	60	60	60	-
	TRNS OXIDE RED AA2005	-	-	-	-	60
	DA705	0.5	0.5	0.5	0.5	0.5
	XYLENE	10	10	10	10	10
Drying condition for the label base layer		250 °C 10 min	250 °C 10 min	250 °C 10 min	250 °C 10 min	250 °C 10 min
Composition of the sticking layer		Same as the label base layer	Same as the label base layer	Same as the label base layer	Same as the label base layer	Same as the label base layer in Ex. 1
Drying condition for the sticking layer		200 °C 5 min	200 °C 5 min	200 °C 5 min	200 °C 5 min	200 °C 5 min

Table 3

		Ex. 11	Ex. 12	Ex. 13
Composition of the label base layer	TYRANNO COAT VS-100	-	-	-
	TYRANNO COAT VN-100	60	30	-
	KR255	20	10	-
	TSR116	20	10	-
	KR-380	-	30	-
	TRNS OXIDE RED AA2005	60	30	-
	DA705	0.5	0.5	-
	XYLENE	10	10	-
Drying condition for the label base layer		250 °C 10 min	250 °C 10 min	250 °C 10 min
Composition of the sticking layer		Same as the label base layer in Ex. 6	Same as the label base layer in Ex. 10	Same as the label base layer in Ex. 10
Drying condition for the sticking layer		200 °C 5 min	200 °C 5 min	200 °C 5 min

Table 4

		Com. Ex. 1	Com. Ex. 2	Com. Ex. 3
Composition of the sticking layer	TYRANNO COAT VS-100	-	-	-
	TYRANNO COAT VN-100	-	-	-
	KR255	60	40	-
	TSR116	-	-	60
	KR-380	30	60	30
	TRNS OXIDE RED AA2005	-	-	-
	DA705	0.5	0.5	0.5
	XYLENE	7	10	13
Drying condition for the sticking layer		150 °C 5 min	150 °C 5 min	150 °C 5 min
Composition of the label base layer		Same as the label base layer in Ex. 1	Same as the label base layer in Ex. 1	Same as the label base layer in Ex. 1
Drying condition for the label base layer		250 °C 10 min	250 °C 10 min	250 °C 10 min

Test Examples

The following tests were conducted using the labels obtained in the above-mentioned Examples and Comparative Examples. The results are shown in Table 5.

High-temperature labeling test 1:

Each label was compressed to an aluminum billet at a side with a surface temperature of 500°C at a pressure of 50 g/cm^2 for 5 seconds using a manually-operated label attaching machine. Thereafter, the aluminum billet was allowed to cool to room temperature, and was observed for label attachment state, appearance and scratch resistance. The results are shown in Table 5.

The label adhesion was evaluated according to the following criteria:

o: The label is not peeled off; and

x: The label is peeled off.

The criteria for evaluating the appearance were as follows:

x: The label base layer is partially peeled off the support; and

o: No change observed.

The scratch resistance was evaluated by scratching the label base layer 2 or 3 times at a speed of 5 cm/second using a coin while applying a load of about 500 g to the coin, and the evaluation criteria were as follows:

x: The label base layer crumbled and peeled off the support; and

o: The label base layer is not scratched or the surface of the layer is slightly peeled off.

High-temperature labeling test 2:

Evaluations were conducted in the same manner as in the high temperature label attachment test 1 except that the surface temperature of the label attaching target is 600°C.

Table 5

	Attachment test 1			Attachment test 2		
	Adhesion	Appearance	Scratch resistance	Adhesion	Appearance	Scratch resistance
Ex. 1	o	o	o	o	o	o
Ex. 2	o	o	o	o	o	o
Ex. 3	o	o	o	o	o	o
Ex. 4	o	o	o	o	o	o
Ex. 5	o	o	o	o	o	o
Ex. 6	o	o	o	o	o	o
Ex. 7	o	o	o	o	o	o
Ex. 8	o	o	o	o	o	o
Ex. 9	o	o	o	o	o	o
Ex. 10	o	o	o	o	o	o
Ex. 11	o	o	o	o	o	o
Ex. 12	o	o	o	o	o	o
Ex. 13	o	-	-	o	-	-
Com. Ex. 1	×	×	×	×	×	×
Com. Ex. 2	×	×	×	×	×	×
Com. Ex. 3	×	×	×	×	×	×

CLAIMS

Claim 1:

A composition for a heat-resistant label comprising a polymetallocarbosilane resin (A), a silicone resin (B), and a solvent (C), wherein the weight ratio of the polymetallocarbosilane resin (A) : the silicone resin (B) is about 1 : about 9 to about 9 : about 1.

Claim 2:

A composition for a heat-resistant label further comprising an inorganic powder (D), wherein the inorganic powder (D) is contained in a ratio of about 0.0001 to about 80 % by weight.

Claim 3:

A composition for a heat-resistant label according to claim 1 or 2, wherein the weight ratio of the polymetallocarbosilane resin (A) : the silicone resin (B) is about 3 : about 7 to about 8 : about 2.

Claim 4:

A composition for a heat-resistant label according to any one of claims 1 to 3, wherein the polymetallocarbosilane resin (A) has a weight-average

molecular weight of about 500 to about 10000.

Claim 5:

A composition for a heat-resistant label according to any one of claims 1 to 4, wherein the silicone resin (B) has a weight-average molecular weight of about 200 to about 5000000.

Claim 6:

A composition for a heat-resistant label according to any one of claims 1 to 5, wherein the polymetallocarbosilane resin (A) is a polytitanocarbosilane resin.

Claim 7:

A heat-resistant label comprising a sticking layer of a hardened coating film obtained by applying a composition according to any one of claims 1 to 6 to one side of a support, and evaporating off the solvent contained in the composition.

Claim 8:

A heat-resistant label according to claims 7, wherein the sticking layer has a thickness of about 5 µm to about 100 µm.

Claim 9:

A heat-resistant label according to claim 7 or 8, wherein the support has a thickness of about 5 μm to about 100 μm.

Claim 10:

A heat-resistant label according to any one of claims 7 to 9, wherein the support is an aluminum foil, stainless steel foil, or copper foil.

Claim 11:

A heat-resistant label according to any one of claims 7 to 10 having a heat-resistant label base layer on the other side of the support.

Claim 12:

A heat-resistant label according to claim 11, wherein the label base layer has a thickness of about 0.5 μm to about 100 μm.

Claim 13:

A heat-resistant label according to claim 11 or 12, wherein the label base layer is a cured coating film obtained by crosslinking the resin in the composition

according to any one of claims 1 to 6.

Claim 14:

A heat-resistant label according to any one of claims 11 to 13 having an identification part on the label base layer.

Claim 15:

An article to which a heat-resistant label of any one of claims 7 to 14 is attached through a cured sticking layer.

Claim 16:

A method for producing a heat-resistant label comprising the steps of:

applying a composition of any one of claims 1 to 6 to one side of a support; and

drying the applied composition to form a hardened coating film.

Claim 17:

A production method according to claim 16, wherein the applied composition is dried at about 50 °C to about 240 °C.

Claim 18:

A production method according to claim 16 or 17, comprising, prior to the step of applying a composition of any one of claims 1 to 6 to one side of a support, the steps of:

applying a composition for a heat-resistant label base layer to the other side of the support; and

drying the applied composition to form a cured coating film.

Claim 19:

A production method according to any one of claims 16 to 18, wherein the composition for a label base layer is a composition of any one of claims 1 to 6.

ABSTRACT

The present invention relates to compositions for heat-resistant labels that are attachable at high-temperature conditions of 300°C or higher, heat-resistant labels, products with the labels attached, and methods for producing the labels. A heat-resistant label having a sticking layer of a hardened coating film made of a composition containing a polymetallocarbosilane resin (A), a silicone resin (B), a solvent (C), and optionally an inorganic powder (D) is attachable at a high-temperature. More specifically, the present invention relates to compositions for heat-resistant labels containing a polymetallocarbosilane resin (A), a silicone resin (B), and a solvent (C), wherein the weight ratio of the polymetallocarbosilane resin (A) : the silicone resin (B) is about 1 : about 9 to about 9 : about 1, heat-resistant labels using such composition, and products with the labels attached thereon.